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## (54) IMPROVEMENTS IN OR RELATING TO PREPARATION OF ALKALINE EARTH SULPHIDES

- (71) We, ARON VECHT, a British citizen, of 95 Corringham Road, London, N.W.11, GERALD BIRD, a British citizen, of 80 Nether Street, London, N.12, and Mahmood Quddus, a citizen of the Republic of Bangladesh, of 37 Ripon Road London, S.E.18, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the preparation of alkaline earth sulphides, that is to say the sulphides of calcium, strontium, barium and magnesium.
- Conventional methods of preparing the alkaline earth sulphides include firing the carbonates in hydrogen sulphide and reducing the sulphates by firing with charcoal. Such methods result in the presence of oxygen in the final product which may have a deleterious effect, particularly in some applications such as where the alkaline earth sulphide is used as a phosphor material.
- It is an object of the invention to provide a method of preparing alkaline earth sulphides which results in a substantially oxygen-free final product.
- According to the invention a method of preparing a sulphide of an alkaline earth metal comprises the steps of dissolving the alkaline earth metal in an alcohol, adding hydrogen sulphide to form the hydrosulphide of the said metal, precipitating the hydrosulphide, and firing the precipitated hydrosulphide to form the sulphide of the said metal.
- Preferably the precipitated hydrosulphide is fired either in an inert or in a sulphurising atmosphere.
- Where the alkaline earth metal is barium the alcohol is preferably ethanol and the precipitated hydrosulphide or barium is preferably fired for about one hour at about 800°C.
- Where the alkaline earth metal is strontium the alcohol is preferably methanol and the precipitated hydrosulphide of strontium is preferably fired for about one hour at about 1000°C.
- Where the alkaline earth metal is calcium the alcohol is preferably methanol and the precipitated hydrosulphide of calcium is preferably fired for about one hour at about 1200°C.
- In order that the invention may be more fully understood reference will now be made to the following examples of carrying out the invention.
- EXAMPLE 1**
- 5 gms of metallic barium is dissolved in 125 mls of ethanol which has been degassed. The clear solution is then filtered and 125 mls of a saturated solution of hydrogen sulphide in ethanol is then dripped in. This results in the precipitation of barium hydrosulphide as a white powder. This is then filtered, washed with acetone and vacuum dried. The dried powder is then fired for one hour at 800°C in an inert or sulphurising atmosphere. The resultant barium sulphide has a brilliant white non-luminescent appearance.
- EXAMPLE 2**
- 5 gms of strontium is dissolved in 200 mls of degassed methanol through which hydrogen sulphide is slowly passed. The rate of solution of the metal rises sharply as the hydrogen sulphide becomes dissolved in the methanol. When saturation point is reached the solution is filtered and then 1000 mls of degassed acetone is added to salt out the strontium hydrosulphide which is then filtered, washed and vacuum dried. The strontium hydrosulphide is then fired for one hour at 1000°C in an inert or sulphurising atmosphere. The strontium sulphide so produced is a brilliant white non-luminescent powder.
- EXAMPLE 3**
- 5 gms of calcium are taken and placed in 100 ml of degassed methanol through which hydrogen sulphide is slowly passed.

The calcium only partially dissolves and the passage of hydrogen sulphide is maintained until the rate of solution of the calcium drops markedly, which takes place after about two hours. The resulting solution is then filtered and 1000 mls of degassed acetone is added to salt out the calcium hydrosulphide which is then filtered, washed and vacuum dried. The calcium hydrosulphide is then fired for one hour at a temperature of 1200°C for about one hour in an inert or sulphurising atmosphere.

The resultant calcium sulphide is a brilliant white non-luminescent material.

In each of the above examples anhydrous hydrosulphides that are produced as intermediate products should not be stored since they are strongly hygroscopic and are sensitive to oxidation.

Alkaline earth sulphides manufactured in accordance with any of the examples described above have a very much reduced degree of oxygen contamination and the final product is a fine powder which is homogeneous and of good quality. They are useful as phosphor materials when suitably activated with impurities.

#### WHAT WE CLAIM IS:—

1. A method of preparing a sulphide of an alkaline earth metal which comprises the steps of dissolving the alkaline earth metal in an alcohol, adding hydrogen sulphide to form the hydrosulphide of the said metal, precipitating the hydrosulphide and firing the precipitated hydrosulphide to form the sulphide of the said metal.

2. A method according to claim 1 wherein the hydrosulphide is precipitated by the addition of the hydrogen sulphide.

3. A method according to claim 1 wherein the hydrosulphide is precipitated by the addition of acetone.

4. A method according to any one of the preceding claims in which the precipitated hydrosulphide is fired in an inert atmosphere.

5. A method according to any one of claims 1 to 3 in which the precipitated hydrosulphide is fired in a sulphurising atmosphere.

6. A method according to any one of the claims 2, 4 as dependent on 1 or 2, or 5 in which the metal is barium and the alcohol is ethanol.

7. A method according to claim 6 in which the precipitated hydrosulphide is fired for about one hour at about 800°C.

8. A method according to any one of claims 2, 4 as dependent on 1 or 2, or 5 in which the metal is strontium and the alcohol is methanol.

9. A method according to claim 8 in which the precipitated hydrosulphide is fired for about one hour at about 1000°C.

10. A method according to any one of claims 3, 4 as dependent on 3, or 5 in which the metal is calcium and the alcohol is methanol.

11. A method according to claim 10 in which the precipitated hydrosulphide is fired for about one hour at about 1200°C.

12. A method of preparing a sulphide of an alkaline earth metal as claimed in claim 1 and substantially as hereinbefore described.

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